Identification of Materials with Axis-Dependent Conduction Polarity

Thesis

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By

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Abstract

Recent research at Ohio State University has identified materials which exhibit p-type and n-type polarity along perpendicular axes, creating a new class of materials described as goniopolar. While nearly all the currently known goniopolar materials are metals, several goniopolar semiconductors have recently been identified. The objective of this investigation was to determine if palladium dichalcogenides, such as PdS_2 and $PdSe_2$, are goniopolar semiconductors. This was done by calculating the band structure of each material using density-functional theory, then finding the thermopower along each axis to identify the charger carriers. $PdSe_2$ exhibited goniopolarity at undoped levels in both the x-z and y-z axes, while PdS_2 exhibited goniopolarity at undoped levels in the x-z axes only. However, though p-type doping, PdS_2 can exhibit goniopolarity in the y-z axes, and $PdSe_2$ can retain goniopolarity for both p-type and n-type doping. The addition of palladium dichalcogenides to the pool of goniopolar semiconductors, and the methods used to identify goniopolarity, has many potential applications in electronic devices.

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Introduction

Semiconductors are an essential technology which have enabled many major advancements over the last few decades, such as diodes, transistors, and solar cells. Several unique properties of semiconductors are a consequence of the interaction between two types of charge carriers: electrons and holes. These are referred to as n-type and p-type semiconductors, respectively. Most semiconductors exhibit only one of these two types, and by combining a p-type and n-type semiconductor a p-n junction is formed, which allows current to flow in only one direction. This is the principle behind diodes. However, new materials have recently been discovered which exhibit p-type and n-type charge carriers along perpendicular axes, in a phenomenon known as goniopolarity [1].

Literature Review

Goniopolar materials have been infrequently reported over the last half-century, but the focus was limited to their “anomalous” transport properties. In recent years, their potential for applications in electronics and thermoelectrics have been identified, renewing academic interest in them. While other materials, known as (p x n)-type, have been designed with layered p-type and n-type superlattices that exhibit opposite polarity thermopowers along perpendicular axes, goniopolarity is unique because it occurs in a single band where the carrier is simultaneously holes or electrons, depending on the

relative orientation of the crystal [1]. Due to the challenges with creating large crystals that can be used to test for axis-dependent carrier polarity, only approximately 14 materials have been experimentally confirmed to show goniopolarity [2]. 12 of these predicted materials are given below in Table 1.

Table 1: Predicted goniopolar materials [2]

Compound	Material Class
CaCuP	Metal
SrCuP	Metal
BaCuP	Metal
BaCuAs	Metal
BaCuSb	Metal
BaAuP	Metal
BaAgP	Semiconductor
LaAuGe	Metal
YCuSi	Metal
LaCuSi	Metal
ScAuSi	Metal
ScAuGe	Metal

The only material that displays a band gap in this list is BaAgP, making it the only semiconductor, while most other goniopolar materials are metals.

Research Significance

As goniopolarity is a relatively recent area of interest, expanding the catalogue of goniopolar materials is essential. Goniopolar materials have potential impacts on nearly

all modern electronic devices, which require integration of materials with different conduction polarities. A single-band, undoped material that exhibits goniopolarity could be used to enable new unique technologies, such as quantum computing, and improve existing ones, such as LEDs, solar cells, and transistors. While most goniopolar materials are metals, semiconductors are of particular interest. Recent research has shown that semiconductors can exhibit goniopolarity in materials such as NaSnAs, proving that computationally designed experiments can lead to new goniopolar semiconductors [3].

Overview

The objective of this investigation is to widen the pool of available goniopolar materials, in addition to establishing and refining techniques that can be used to identify which materials exhibit goniopolarity. One class of semiconductors, palladium dichalcogenides, was studied for goniopolarity in this work due to molecular orbital fingerprints and DFT calculations similar to other known goniopolar materials [2]. PdSe2 and PdS_2 were investigated for goniopolarity using simulations to calculate the charge carrier polarity along each axis and determine if axis-dependent conduction polarity occurred.

Methodology

To identify if goniopolarity exists in $PdSe_2$ and PdS_2, the charge carriers along each axis needed to be identified. For goniopolar materials, the charge carriers would exhibit opposite polarity in perpendicular axes, indicating that both holes and free electrons served as charge carriers. The charge carriers were identified by calculating the Seebeck coefficient, or thermopower, along each axis as a function of energy. Thermopower is a measure of the induced voltage in response to a temperature difference, and the sign of thermopower indicates the polarity of charge carriers.

To calculate the thermopower along each axis, first the band structure of each material needed to be calculated. This was accomplished using the Vienna ab Initio Simulation Package (VASP), a density-functional theory (DFT)-based software package [4]. For each system being studied, the crystallographic info was obtained from Materials Project [5]. The system was first relaxed in VASP, using a default mesh of gamma-centered k-points, to allow the system to achieve equilibrium. The relaxed crystal structure was then used to generate a set of k-points that would utilize symmetry to identify the irreducible Brillouin zone, then use its corner points and edges to create input k-point paths in reciprocal space, using a python package named sumo [6]. VASP was then used to calculate the band structure of each material from the sumo-generated k-points file and relaxed crystal structure, and the band structures were plotted using sumo.

Due to the intensity of the necessary calculations, the Ohio Supercomputing Center (OSC) high performance clusters were used for the VASP runs. Calculations which took hours on OSC would have taken days on a personal computer, therefore allowing for much quicker results.

After obtaining the band structures, the thermopower needed to be extracted along each axis. This was done using BoltzTraP2, a code used to obtain transport data from density-functional theory results using smoothed Fourier interpolation [7]. This allowed for calculation of thermopowers along each axis as a function of both temperature and energy. The temperature was kept fixed at 300 K, and the energies were shifted to isolate regions near the middle of the band gap. This data was plotted using a MATLAB script that identifies energy levels where goniopolarity exists.

Results

The band structures and thermopower plots for each material system were calculated using the methods described in the procedure.

Palladium selenide ($PdSe_2$)

The band structure for $PdSe_2$, calculated using VASP and plotted using sumo, is given below in Figure 1.

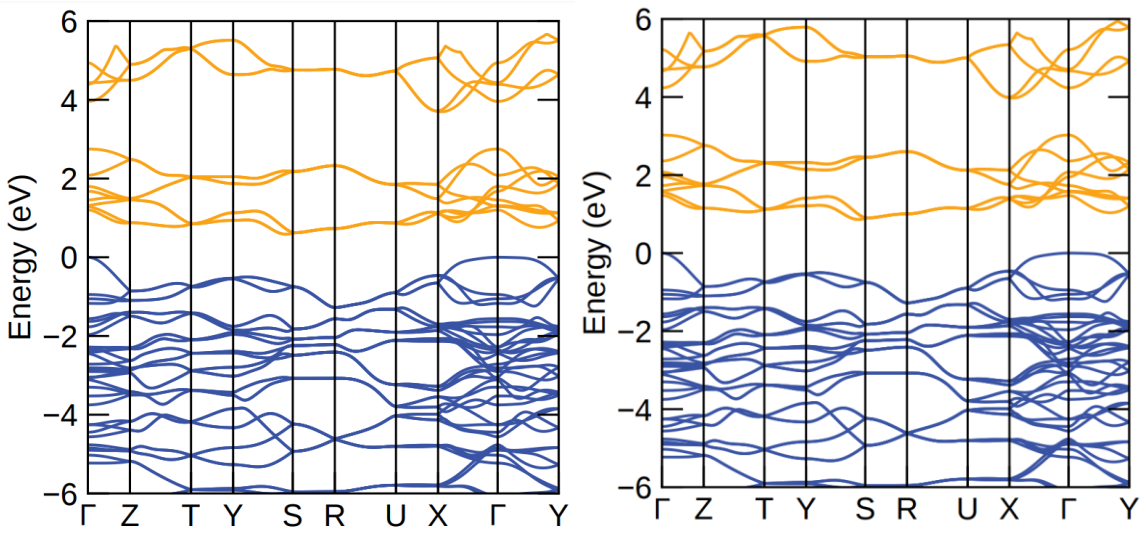

Figure 1. Band structure for $PdSe_2$ (left) before scissor and (right) after scissor

The valence bands are plotted in blue, while the conduction bands are plotted in yellow. This band structure was compared to previously calculated band structures for this material, found in literature, and it was observed that the currently calculated band

structure resembled the established one. From this plot, the indirect band gap was estimated to be 0.54 eV. Compared to the established value of 1.4 eV, this is a severe underestimate; however, this can be identified as a consequence of DFT. DFT tends to underestimate band gaps, and therefore more advanced physics are needed to obtain an accurate band gap. This could include many-body perturbation theory, or the use of hybrid functionals within VASP. These methods were tested but due to the large computational demands were not completed as part of this work. However, goniopolarity is dependent on the curvature of the bands, not the band gap, and this information is present in DFT and can still be used. To create a band structure that closer resembled those found in literature, the band gap was shifted to the correct size using sumo, keeping the band shape but shifting the conduction band to higher energy levels. The thermopower along each axis, and regions where goniopolarity exists, are given below in Figure 2.

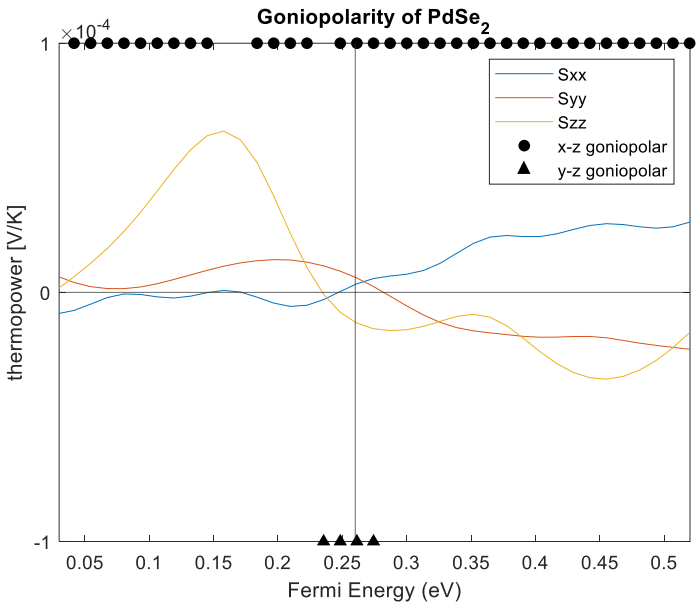

Figure 2. Thermopower plot for $PdSe_2$ at 300 K

From this plot of the thermopower along each axis, at energies near the band gap, goniopolarity can be observed for nearly every energy level. This indicates that $PdSe_2$ is an excellent candidate for goniopolarity, though experimental verification is needed. The region of most interest is the middle of the band gap, which is marked with a vertical line. This is the undoped Fermi level, and in this region goniopolarity is observed along both the x-z and y-z sets of axes. As the material is doped the Fermi level shifts, and either p-type or n-type doping will generally result in goniopolarity in the x-z set of axes, but not in the y-z set.

Palladium sulfide (PdS_2)

Similarly, the band structure for PdS_2 was calculated using VASP and plotted using sumo and is given below in Figure 3.

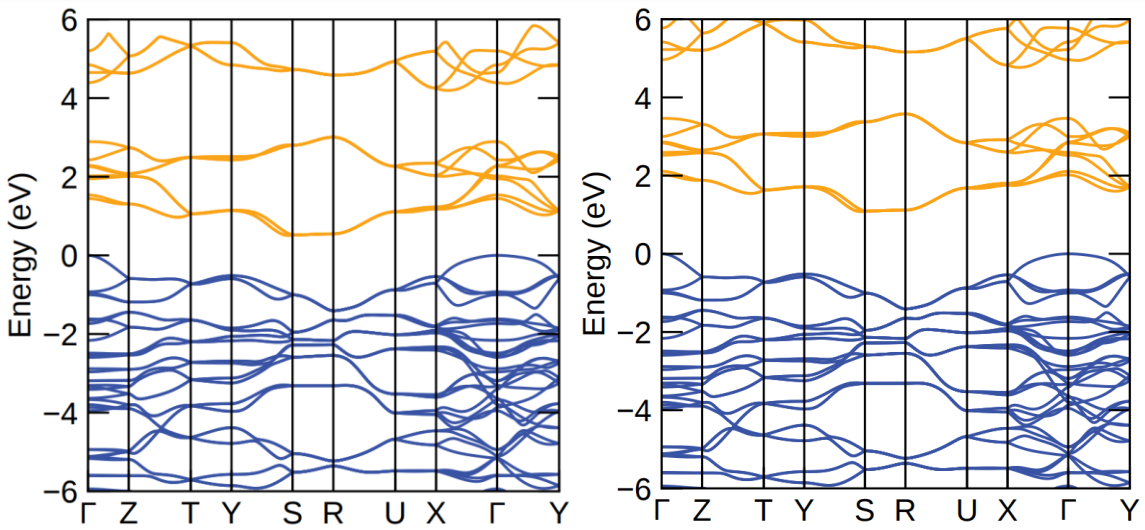

Figure 3. Band Structure for PdS_2 (left) before scissor and (right) after scissor

From this band structure, the indirect band gap was estimated to be 0.52 eV, which is again an underestimate of the literature value of 1.60 eV as a consequence of DFT. This was shifted using a scissor operation in sumo in Figure 3b. Like $PdSe_2$, the band curvature resembles the literature values, and therefore can be used as an indicator of goniopolarity. From this plot, the thermopower values along each axis, close to the band gap, are given below in Figure 4.

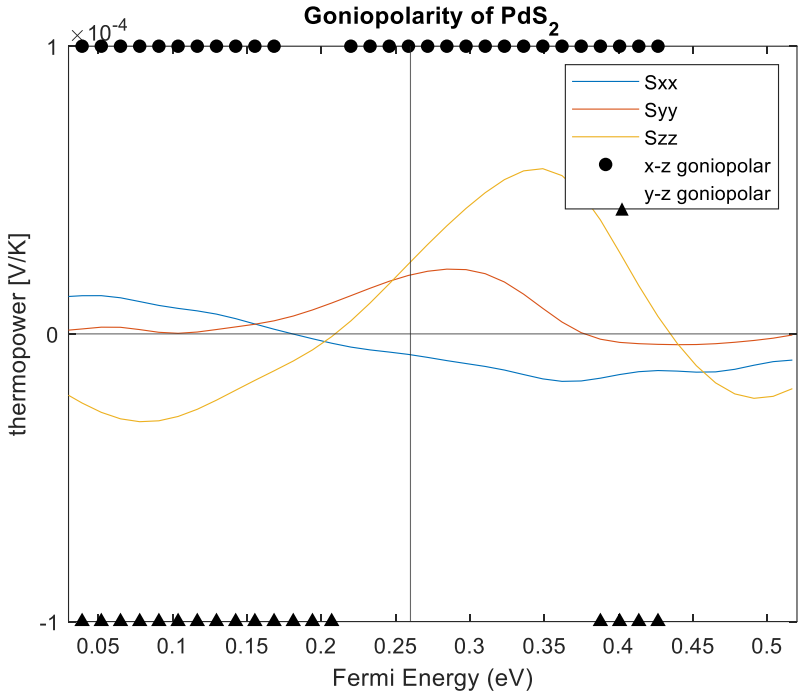

Figure 4. Thermopower plot for PdS_2 at 300 K

This plot indicates that PdS_2 is also a candidate for goniopolarity because it exhibits both positive and negative thermopowers along different axes at the same energy levels. At the undoped Fermi level, marked by the vertical line, goniopolarity is observed in the x-z axes. To achieve goniopolarity in the y-z axes, the material should be p-type doped to introduce extra hole energy levels and lower the Fermi level.

Conclusions

The purpose of this experiment was to determine if palladium dichalcogenides like PdS_2 and $PdSe_2$ exhibited axis-dependent conduction polarity, known as goniopolarity. This was done by calculating the band structure using VASP and analyzing the thermopower along each axis using BoltzTraP2. A MATLAB script was then used to identify Fermi energy levels where goniopolarity occurred. In $PdSe_2$, goniopolarity was observed along both x-z and y-z sets of axes in the undoped semiconductor, and goniopolarity was retained for both p-type and n-type doping. For PdS_2, goniopolarity was observed in the x-z plane at undoped levels; however, p-type doping would yield goniopolarity in the y-z axes as well. This work provides two more promising semiconductor candidates for goniopolarity. To further test these materials, more accurate simulations could be performed, by using lower energy cutoffs, hybrid functionals to obtain more realistic band gaps, and finer energy resolution in BoltzTraP2 to identify more energy levels where goniopolarity may exist. In addition, experimental fabrication of these systems would be useful to validate their goniopolarity outside of a simulation.

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